

## Chemiluminescent Reactions of Excited Helium with Nitrogen and Oxygen

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## Abstract

Active species created in a fast flow of helium by a microwave discharge react outside the discharge with nitrogen or oxygen causing the emission of visible bands of  $N_2$  and  $O_2$ . The emission intensity of these bands decays exponentially with distance, and the decay coefficient depends on both the flow rate of helium and the flow rate of nitrogen or oxygen. At constant flow rate of helium the decay coefficient increases with increasing flow rate of added gas, but the dependence is less than linear. A theoretical analysis of the flow system predicts the exponential decay and a linear dependence between the decay coefficient and the flow rate of added gas. Comparison of the experimental and theoretical results permits the calculation of approximate values of the rate constants for the reactions populating the emitting states and the diffusion coefficients of the excited helium species. A plausible explanation and a means for removing the discrepancy between the experimental and theoretical results are suggested.

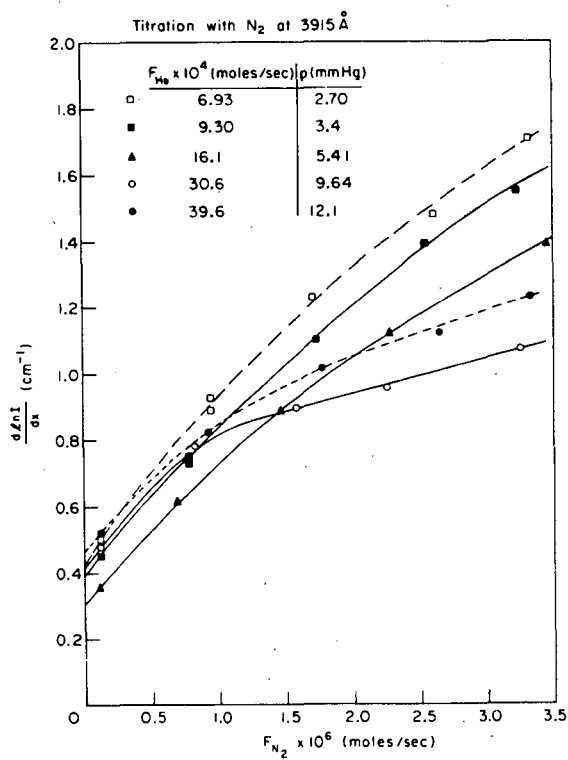
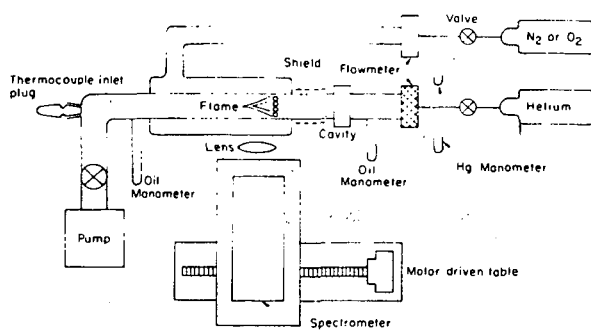
## Introduction

Long lived reactive species, produced when helium gas is subjected to an electrical discharge, react with many other gases and generate characteristic emissions of visible light. The nature of some of these chemiluminescent reactions has been discussed recently in a number of papers.<sup>1-3</sup> The reaction with nitrogen gas produces an intense bright blue flame consisting of the first negative system of  $N_2^+(B^2\Sigma^+ \rightarrow X^2\Sigma^+)$ . With oxygen a bright yellow-green flame is observed due to the excitation of both the first negative system of  $O_2^+(b^4\Sigma^- \rightarrow a^4\Pi)$  and the second negative system of  $O_2^+(A^2\Pi \rightarrow X^2\Pi)$ . In this paper we report the results of our measurements of the special variation of the emission intensity in a fast flow system for various flow conditions, and show how these measurements can be used to evaluate the rate constants for the reactions populating the emitting states.

**Apparatus.** The reaction cell and associated equipment are shown schematically in Fig. 1. The reaction cell consisted of a pair of concentric pyrex tubes 13 and 25 mm o.d. Helium flowed through the inner tube. The titrating gas was introduced into the helium stream via the outer tube through eight 1 mm diameter holes located symmetrically in the wall of the inner tube. High velocity flows of about  $10^4$  cm/sec were maintained by a mechanical vacuum pump rated at 425 liters/sec. The flow rates of the gases were measured using a pair of calibrated critical velocity orifice flowmeters described by Andersen and Friedman.<sup>4</sup> The pressure in the reaction cell was taken as the average value measured by two oil manometers located approximately 20 cm upstream and downstream from the flame zone. The temperature was determined in separate experiments by means of a fine wire thermocouple sealed from the outside with black wax. The observed temperature was determined primarily by the pressure of helium in the discharge, and was nearly independent of the nature and flow rate of the added gas.

The discharge in the helium stream was excited by a 2450 Mc/sec cavity of the Evenson type<sup>5</sup> powered by a 125 W Raytheon diathermy unit. The cavity was located 85 mm upstream of the injection holes. A metal shield excluded the active discharge from extending into the flame zone.

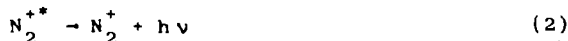
Spectra and intensity measurements were made with a 500 mm Jarrell-Ash Ebert spectrophotometer using an RCA 1P21 photomultiplier tube. A pair of large condensing lenses served to focus the image of a cross-section of the flame on the entrance slit. The spectrophotometer was mounted on a table which could be moved at constant speed parallel to the axis of the tube. In this way the intensity of the flame was recorded as a function of distance along the tube.



All gases were taken directly from the commercially available high pressure cylinders. The stated concentration of impurities in the helium tanks was 50 ppm, with  $N_2$  being the major contaminant.

#### Interpretation of Data

We assume that an excited helium species  $X^*$  reacts with  $N_2$  or  $O_2$  to give the electronically excited  $N_2^+$  or  $O_2^+$ , and the latter immediately decays by emitting a quantum of light, as indicated by reactions (1) and (2)



At this point the identity of  $X^*$  remains unspecified.  $X^*$  could be for example metastable  $2^3S$  helium atom, in which case  $X$  represents a ground state He atom plus an electron. Alternatively  $X$  could be the  $He_2^+$  molecule, and  $X$  would then represent two ground state helium atoms. For simplicity we assume that under any one set of conditions only one excited helium species is dominant, although we can expect several processes occurring simultaneously. The natural lifetime of  $N_2^+$  or  $O_2^+$  is short compared with the time scale of the experiment, and thus the emission intensity is proportional to the rate of reaction (1). If the concentration of nitrogen is uniform and constant along the tube, which should be the case after some distance of travel to effect complete mixing, the decay in intensity with distance should parallel the decay in concentration of  $X$ . We therefore need to derive an expression for the concentration of  $X$  as a function of position.

We consider a semi-infinite cylinder of radius  $r_0$ . Let  $n$  be the concentration of  $X$  and  $N$  the concentration of the added gas, say  $N_2$ . We assume that the two major mechanisms responsible for the decay of  $n$  are diffusion of  $X$  to the walls where  $n=0$  and the chemical reaction represented by Eq. (1). Under these conditions the rate of change of  $n$  is given by

$$u \frac{\partial n}{\partial x} = D \nabla^2 n - kNn \quad (3)$$

where  $u$  is the stream flow velocity,  $x$  is the axial coordinate,  $D$  is the diffusion coefficient of  $X$ , and  $k$  is the specific rate constant for reaction (1). Since transport along the axial direction by convection is much greater than by diffusion, we need only consider radial diffusion, and for this case the solution of the axial part of Eq. (3) is

$$\bar{n}(x) = n_0 \exp \left[ - \left( \frac{D}{\Lambda^2} + kN \right) \frac{x}{u} \right] \quad (4)$$

$\Lambda$ , the characteristic diffusion length given by  $\Lambda = r_0/2.405$ , is obtained from the solution of the radial part of Eq. (3) using the assumed boundary condition  $n=0$  at the walls. The radial dependence of  $\bar{n}(x)$  is taken care by the experimental arrangement, since the photomultiplier tube views an entire cross-section of the flame, and its response is proportional to the average intensity. The flow velocity  $u$  and the concentration  $N$  are calculated by Eqs. (5) and (6)

$$u = RT\dot{V}/p\pi r_0^2 \quad (5)$$

$$N = (F_N/\dot{V})(p/RT) \quad (6)$$

where  $p$  is the pressure,  $T$  is the temperature,  $F_N$  is the flow rate of the added gas in moles/sec, and  $\dot{V}$  is the total flow rate, which in these experiments is essentially equal to the flow rate of helium. If the emitted intensity  $I(x)$  is proportional to  $\bar{n}(x)$ , it follows that a plot of  $\ln I$  vs.  $x$  should be a straight line with slope

$$-\frac{d \ln I}{dx} \equiv S = \frac{(D_0 p_0)(2.405)^2 \pi}{760 \dot{V} RT} + k\pi \left( \frac{p r_0}{\dot{V} RT} \right)^2 F_N \quad (7)$$

In Eq (7) we make use of the fact that  $D$  is inversely proportional to pressure and  $(D_0 p_0)$  is the diffusion coefficient at pressure 1 mm Hg. Using Eq (8) it

should be possible to evaluate  $k$  and  $D_0 p_0$  from the variation of  $S$  with flow rate of added gas.

### Results

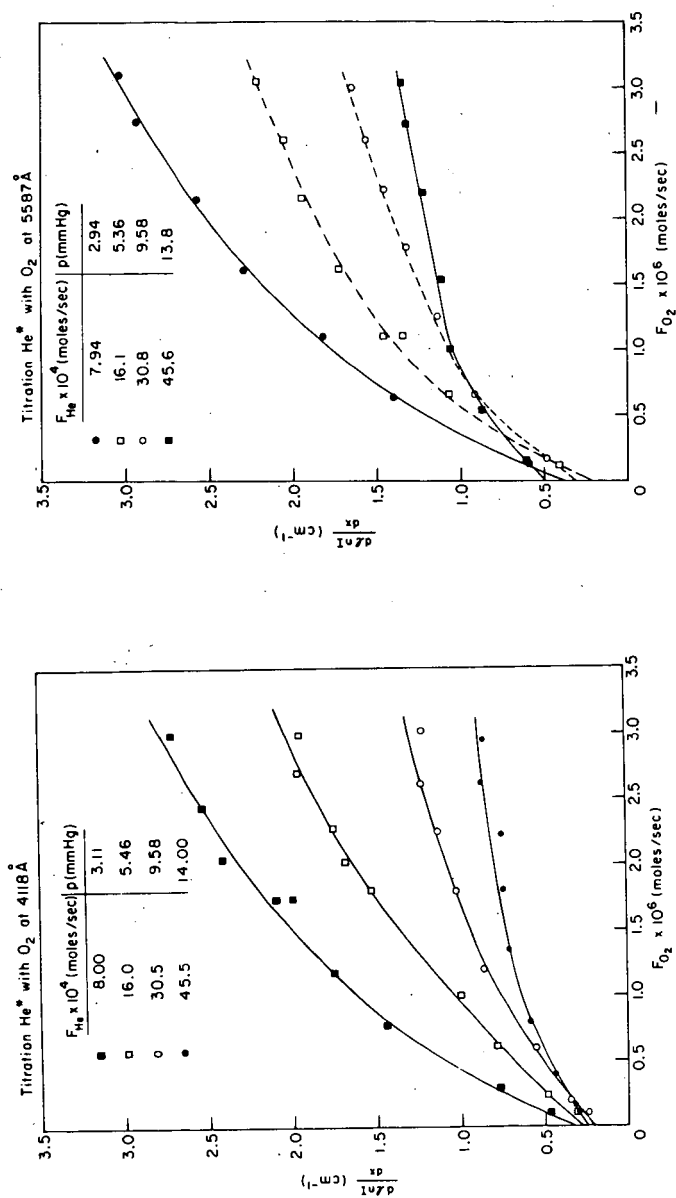
Measurements of intensity vs. distance were recorded for nitrogen at 3915 Å and for oxygen at 5587 Å and 4116 Å. These wave lengths are the heads of intense vibrational bands of the first negative system of  $N_2^+$  and the first and second negative systems of  $O_2^+$ . Typical flames were 2-10 cm in length, and over this distance the intensity varied by nearly a factor of 100. Plots of the logarithm of intensity vs. distance demonstrated a linear behavior over a 50 fold change in intensity, as predicted from Eq (7). Negative deviations from linearity occurred in the region within 0.5-1.0 cm from the injection ports, this no doubt resulting from incomplete mixing of the reactive gases. The slopes of the linear portions were plotted against the flow rate of the added gas, and the results are shown in Figs. 2-4. It is evident that these curves are not linear over the range of flow rates covered, as expected from Eq. 8, but rather show a pronounced downward curvature. We have provisionally taken the extrapolated intercepts and the initial slopes and used them together with Eq. (7) to compute the reaction rate constant as well as the diffusion coefficient of the excited species  $X$ . The results are shown in Table I. The magnitude of the rate constants for the nitrogen and oxygen reactions are comparable and in the range of  $10^{13}$  cc mole<sup>-1</sup> sec<sup>-1</sup>. These rate constants are very fast indeed being of the order of the collision frequency. The diffusion coefficients are of the right order of magnitude for any one of the excited helium species, but the observed temperature dependence is clearly too steep.

### Discussion

The procedure of using initial slopes to evaluate the rate constants in Table I is admittedly questionable in view of the fact that the curves in Figs. 2-4 do not fit well the model embodied in Eq. (8). Although the intensity of the flames does decay exponentially with distance, and the decay coefficient increases with increasing flow rate of added gas, the increase is not linear. Deviations from linearity appear to be more pronounced at higher pressures (i.e. higher flow rates of helium), presumably because of slower mixing of the reactive streams. This suggests that incomplete mixing and non-uniform concentration of added gas may be responsible for the breakdown of the model, even though the method of injecting the second gas into the helium stream with an initial radial component of velocity should encourage fast mixing. At the lower flow rates of added gas the intensity of the flame decays less rapidly, and consequently intensity measurements are made farther away from the inlet of the second gas. Under these conditions we expect mixing to be more nearly complete and this is in fact the rationale for using the initial part of the curves for evaluating the rate constants. We can check whether incomplete mixing is indeed the source of our difficulties by changing the size of the inlet holes and seeing whether the intensity profiles are affected. We are currently carrying out these experiments.

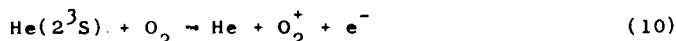
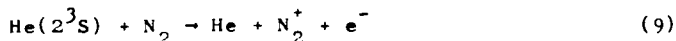
We have not considered so far the identity of the excited helium species  $X$ . Collins and Robertson have shown that the upper state of  $N_2^+$  giving rise to the blue emission is populated by reaction of  $N_2$  with both metastable  $2^3S$  He and  $He_2^+$ . Similarly they have shown that the upper states of both band systems of  $O_2^+$  are populated by reaction of  $O_2$  with  $2^3S$  He, and in addition the upper state of the 5587 Å system is also populated by  $He_2^+$ . Differences in the  $O_2$  titration curves for the two band systems, particularly with regard to the diffusion coefficients at high pressures when  $He_2^+$  is dominant, may result from the fact that different species give rise to the emission. More accurate measurements of the diffusion coefficient are necessary to resolve this point.

There are very few measurements of the rate constants for these reactions with which we may compare our results. Fehsenfeld and co-workers report a rate constant of  $4 \times 10^{14}$  cc mole<sup>-1</sup> sec for reaction (8)





while Sholette and Muschlitz<sup>9</sup> give values of  $5 \times 10^{13}$  and  $11 \times 10^{13}$  cc mole<sup>-1</sup> sec<sup>-1</sup> for the reactions (1) and (10)



Our preliminary results are in quite reasonable agreement.

#### References

1. C. B. Collins and W. W. Robertson, J. Chem. Phys. 40, 701 (1964); 40, 202 (1964); 40, 2208 (1964).
2. A. L. Schmeltekopf and H. P. Broida, J. Chem. Phys. 39, 1261 (1963).
3. E. E. Ferguson, F. C. Fehsenfeld, P. D. Goldan, A. L. Schmeltekopf, and H. I. Schiff, Planetary Space Sci. 13, 823 (1965).
4. J. W. Andersen and R. Friedman, Rev. Sci. Just. 20, 61 (1949).
5. F. C. Fehsenfeld, K. M. Evenson, and H. P. Broida, Rev. Sci. Just. 36, 294 (1965).
6. E. W. McDaniel, Collision Processes in Ionized Gases (John Wiley & Sons, Inc., New York, 1964), p. 503.
7. Ibid, p. 516.
8. F. C. Fehsenfeld, A. L. Schmeltekopf, P. D. Goldan, H. I. Schiff, and E. E. Ferguson, J. Chem. Phys. 44, 4087 (1966).
9. W. P. Sholette and E. E. Muschlitz, J. Chem. Phys. 36, 3368 (1965).

Table I

#### a. Titration with N<sub>2</sub> at 3915 Å

Run	$F_{\text{He}} \times 10^4$ moles/sec	p mm Hg	T °K	$k \times 10^{-13}$ cc mole <sup>-1</sup> sec <sup>-1</sup>	$\frac{D P}{Q_0}$ (cm <sup>2</sup> sec <sup>-1</sup> )(mm Hg)
1	6.93	2.70	363	2.1	374
2	9.30	3.46	376	2.0	480
3	16.1	5.41	413	2.8	696
4	30.6	9.64	480	4.2	2140
5	39.6	12.1	508	4.4	3310

#### b. Titration with O<sub>2</sub> at 5587 (First negative system of O<sub>2</sub><sup>+</sup>)

6	7.94	2.99	370	6.7	403
7	16.1	5.36	409	8.4	543
8	30.8	9.58	475	9.0	1660
9	45.6	13.8	515	8.3	4030

#### c. Titration with O<sub>2</sub> at 4118 (Second negative system of O<sub>2</sub><sup>+</sup>)

10	8.00	3.11	366	5.7	331
11	16.1	5.40	418	5.3	643
12	30.5	9.58	488	6.4	1020
13	45.5	14.0	526	5.1	2140